Oxidative Alkaline Leaching of Americium from Simulated High-Level Waste Sludges

Wendy A. Reed[a], Alexander Yu. Garnov[a], Linfeng Rao*[a], Kenneth L. Nash[b,c] and Andrew H. Bond[b,d]

[a] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

[b] Chemistry Division, Argonne National Laboratory, Argonne, IL

* Corresponding author phone: 1-510-486-5427; fax: 1-510-486-5596; e-mail: LRao@lbl.gov

[c] Present Address, Chemistry Department, Washington State University, Pullman, WA 99164-4630

[d] Present Address: PG Research Foundation, 8205 Cass Avenue, Suite 111, Darien, IL 60561

Abstract

Prior to vitrification, the nuclear waste sludges in underground tanks that were generated during the operation of the plutonium production processes BiPO$_4$, Redox and PUREX are to be treated to remove some of the problematic non-radioactive elements. Alkaline oxidative leaching has been proposed as the appropriate pretreatment to enhance chromium removal from the sludge phase. Because the light actinides also are present in the sludge and characterized by diverse redox chemistry, the effect of such a procedure on the actinide speciation in the sludges must be examined. We have studied the leaching behavior of americium from sludge simulants using potassium permanganate, potassiumpersulfate, and sodium ferrate in alkaline solution. Up to 60% of americium sorbed onto the simulants is leached from the sludges by alkaline persulfate and permanganate, while ferrate has minimal impact on americium dissolution. The percentage of americium leached increases with [NaOH] (between 1.0 and 5.0 M). The initial rate of americium leaching by potassium persulfate increases in the order BiPO$_4$ < Redox < PUREX, though effects related to americium redox chemistry, the stability of persulfate, composition of the sludges, and surface sorption phenomena complicate interpretations of the rate data. The data are most consistent with oxidation of Am^{3+} in the sludge to either AmO$_2^+$ or AmO$_2^{2+}$ in solution. Though neither of these species is expected to exhibit long-term stability, the potential for mobilization of americium from sludge samples would have to be accommodated in the design of any oxidative leaching process for real sludge samples.

Introduction

Large quantities of nuclear wastes remain in underground tanks across the U.S. Department of Energy complex. At the Hanford Site in Washington, a total of 177 underground tanks contain 1.4×10^5 m^3 of wastes with 1.7×10^8 curies of radioactivity (1). These wastes were generated during a period of more than 40 years of industrial-scale reprocessing of spent nuclear fuel to produce plutonium (2, 3). The acidic effluents of the reprocessing schemes were made alkaline to reduce corrosion of the mild steel linings of the tanks and to precipitate metal hydroxides. After a few decades of storage, the nuclear wastes in the Hanford tanks have stratified into three layers: salt cake (primarily water-soluble sodium salts), supernatant liquid and solid sludge. The densest layer is the metal oxide/hydroxide sludge. This material contains the majority of the actinide elements and other radionuclides and so represents most of the high level waste (HLW) in the tanks. The current strategy for the management of these wastes calls for the vitrification of HLW sludge prior to disposal in a mined geologic repository (4).

Besides the radioactive materials, the sludge also contains large amounts of non-radioactive components like aluminum and sodium. Since the vitrification process is very costly (it is estimated that a canister of vitrified high level waste will cost $1 million), pretreatment of the sludge is desirable to remove as many of the non-radioactive constituents as is practical thus minimizing the volume of glass produced. Some of the non-radioactive elements in the sludge are considered "problematic" in the vitrification process. For example, the presence of chromium in the sludge could result in the formation of spinel-type crystalline phases in the glass melter at the designed operation temperature (1050°C). Crystalline inclusions will adversely affect the vitrification process

and reduce the integrity of the glass (5). To reduce the possibility of forming these phases, the concentration of chromium in the feed to the vitrification plant must be controlled. Alkaline scrubbing has proven reasonably effective for removing aluminum by converting aluminum oxides/hydroxides into soluble aluminates (6). This treatment is less effective for the removal of chromium. As an alternative, leaching the sludge with alkaline solutions containing oxidants ("oxidative alkaline leaching") has been proposed and tested. A previous study has shown that ferrate and permanganate effectively remove chromium from the sludge by oxidizing insoluble Cr(III) to soluble Cr(VI) (3).

Before the oxidative leaching can be reliably utilized in sludge pretreatment, the effect of oxidants on the radionuclides in the sludge, actinides in particular, must be investigated. Treating the sludge with oxidative alkaline leachates could generate conditions under which normally insoluble actinides (e.g., Am(III), Pu(IV) and Np(IV)) can no longer be reliably assumed to remain in the sludge phase. In fact, it has been reported that the concentration of plutonium in the leachate was increased in oxidative leaching (7). Clearly this is an adverse outcome, as the purpose of sludge washing is to remove the non-radioactive and/or problematic elements while concentrating the actinides in the sludge. A preliminary study from this group also shows that the presence of $K_2S_2O_8$ could increase the concentration of americium in the leachate of $BiPO_4$ sludge by 10-20% at $85^{\circ}C$ (8). These preliminary and limited data (7,8) indicate that a comprehensive understanding of the chemical behavior of actinides (americium and plutonium in particular) in oxidative alkaline leaching is critical to the development of the strategies for HLW sludge pretreatment.

The HLW sludges at Hanford contain a variety of wastes from different reprocessing schemes including the $BiPO_4$ co-precipitation process, and the Redox and PUREX solvent extraction processes. As a result of the use of several primary separation processes and the practice of evaporating and mixing wastes between tanks to optimize the use of available space, the radionuclides in the sludge in a given tank could well exist in different chemical environments and thus demonstrate different chemical behaviors during sludge washing. A previous study on the leaching of uranium (8) suggests that uranium may be associated with phosphate in the $BiPO_4$ sludge, but exist as hydrous oxides in the Redox sludge. In the present work, the effect of $K_2S_2O_8^{2-}$, $KMnO_4^-$ and $Na_2FeO_4^{2-}$ on the leaching of ericium from different sludge simulants is characterized.

Experimental

Chemicals and equipment. Deionized water from a MilliQ system was used to prepare all solutions. NaOH, HNO_3, HCl, $KMnO_4$ and $K_2S_2O_8$ were of reagent grade and used as received. Sodium ferrate was synthesized using a procedure modified from a method in the literature (9). [243]Am was obtained from the inventory at Lawrence Berkeley National Laboratory and purified by cation exchange. The purity of the [243]Am solution was confirmed by α-spectroscopy with only two peaks at 5.28 Mev (88%) and 5.23 Mev (11%) observed. A stock solution of Am(III) in 0.5 M HNO_3 was prepared. The α-activity in the samples was measured using a Perkin Elmer Liquid Scintillation counter (model number 1414). The scintillation cocktail Ecolume (ICN Biomedicals) was used for liquid scintillation counting (LSC).

Sludge preparation and leaching. Four simulated sludges (BiPO$_4$, modified BiPO$_4$, Redox and Purex sludges) were prepared at Argonne National Laboratory based on the formulae reported by Kupfer (4). Detailed information on the composition of the sludges is provided in an earlier report (10). The oxidative leaching experiments were conducted in two steps: 1) sorption of Am(III) onto the sludge from a solution designed to simulate the waste tank supernatant; 2) leaching the americium from the sludge with alkaline solutions in the presence of various oxidants.

In the first step, approximately 0.05 g of each of the sludges was contacted with 4 ml of 0.1 M Na$_2$CO$_3$/0.5 M NaOH/1 M NaNO$_3$ solution (which is representative of the supernatant solution in Hanford tanks) containing tracer levels of [243]Am (typically between 0.1 and 0.4 μCi) in 15 ml polyethylene centrifuge tubes. The plastic tubes were used instead of glass vessels because a previous study has shown that americium is sorbed onto the surface of borosilicate glass under alkaline conditions (11). The tubes were shaken for a period of at least 24 hours to allow sufficient time for the americium to be sorbed onto the sludge. The samples were centrifuged and the α-activity of the supernatant was determined by liquid scintillation counting. It was found that 95% of the americium was sorbed onto the Redox and PUREX sludges (K$_d$ ≈ 7600 ml/g), and 99% onto the BiPO$_4$ sludges (K$_d$ ≈ 8000 ml/g). The supernatant was then discarded and the sludges loaded with americium retained in the centrifuge tubes. This surface-sorbed americium is representative of a substantial fraction of the americium likely present in actual sludge samples. Our experiments do not permit us to distinguish between sorbed and coprecipitated americium that could be present in the actual sludge samples. This fine distinction may also be irrelevant, as the objective of oxidative leaching is to achieve

matrix disruption due to significant penetration of the oxidant into the matrix. If useful penetration is achieved, sorbed and coprecipitated americium will be equally vulnerable to oxidative leaching in actual sludge samples. Quantitative dissolution of all americium present in the sludge sample into the 4 ml of leachate would produce a solution 1.4×10^{-6} M in americium.

In the second step, 4 ml of leaching solution with appropriate concentrations of NaOH and oxidant were added to each tube containing the sludge spiked with americium. The samples were shaken for varying periods of time and centrifuged. Aliquots of the supernatant solution were taken and analyzed by LSC to determine the amount of americium leached from the sludges. The leaching experiments were conducted with solutions of 1, 3 and 5 M NaOH. Three oxidants ($K_2S_2O_8^{2-}$, $KMnO_4^-$ and $NaFeO_4^{2-}$) were studied. The concentration of oxidant was 0.1 M in most experiments. For the leaching of americium from the $BiPO_4$ sludge with alkaline $KMnO_4$ and (separately) $K_2S_2O_8$, parallel experiments were conducted at 25 and 70^oC to evaluate the effect of temperature.

The presence of the oxidants ($KMnO_4$ in particular) and large amounts of NaOH could affect the LSC counting by color quenching and chemiluminescence. To reduce this effect, the samples for LSC were acidified with HNO_3 or HCl before mixing with the scintillation cocktail. For the sample containing $KMnO_4$, it was necessary to "bleach" the sample by adding a few drops of hydrogen peroxide after acidification with HCl. The resulting colorless acidic solution was mixed with the LSC cocktail for α-counting and the efficiency was found to be satisfactory. Duplicate samples were taken to improve counting accuracy. The difference in count rate for duplicate samples was found to be typically 1-2 %. Control samples that contain the amount of americium equivalent to

100% leaching in the corresponding solutions of NaOH and oxidants were also counted by LSC. The percentages of americium leached from the sludges were calculated against the counting results of the control samples.

To check the mass balance of americium in the sorption and leaching experiments, the amount of americium sorbed onto the inner wall of the tubes was checked by removing the suspensions from the tubes and washing the tubes with 6 M HNO$_3$. The amount of americium in the nitric acid washing accounted less than 1-2 % of total americium, suggesting the sorption on the wall was insignificant. In a limited number of multiple-step leaching experiments that are discussed in subsequent sections, the recovery of americium is higher than 95%, confirming that the mass balance of americium in the experiments was satisfactory.

Results

Oxidative alkaline leaching with potassium persulfate (K$_2$S$_2$O$_8$). Potassium persulfate is known to be a strong oxidant in basic solutions, though one with significant kinetic limitations. Previous studies (15-18) suggest that intermediate products (SO$_4^-$, OH and HS$_2$O$_8^-$) rather than persulfate itself are responsible for oxidation under most conditions. The primary redox reaction (19),

$$S_2O_8^= + 2e- \rightarrow 2\ SO_4^=, E° = 2.0V \tag{1}$$
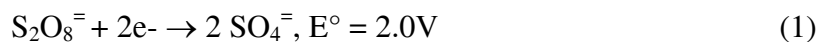
is pH independent in neutral-alkaline solutions, hence the thermodynamic oxidizing power should not change with pH. However, it is known that strong bases cause the catalytic decomposition of S$_2$O$_8^{2-}$ (20), hence higher concentrations of more reactive species may be available at higher [NaOH] leading to possible significant differences in

kinetic behavior. Noble metals (Ag^+ in particular) are known to catalyze persulfate oxidation, probably through the creation of unstable intermediates like Ag^{2+}. As silver, palladium, and rhodium are fission products of significance and certainly present in tank wastes, such catalytic reactions might assume an important role during persulfate oxidation of actual sludges (these metals are not present in the simulant sludge samples).

Introduction of persulfate into an alkaline solution contacting an Am(III)-containing $BiPO_4$ sludge (prepared as described above) results in patterns of enhanced release of americium to the solution (leachate) phase, as shown in Table 1. We focused on $BiPO_4$ sludges for this profiling because current best evidence indicates that this type of sludge should have the highest concentration of transuranic elements (TRU's). Data in Table 1 show that increased base concentration leads to greater americium leaching. The effect of temperature is comparatively limited. Leaching of the spiked $BiPO_4$ sludge with $K_2S_2O_8$ and 3 - 5 M NaOH achieves a pseudo-steady state of about 40% americium leached over a period of several hours.

To assess the impact of the composition of the sludge sample has on the rate of americium leaching by potassium persulfate, we also examined persulfate-enhanced leaching of americium from PUREX, Redox, and $BiPO_4$ modified sludge simulant samples at 25°C. Whereas the $BiPO_4$ sludge consists primarily of phosphate, fluoride and nitrate species, the Redox sludge is composed primarily of aluminum, chromium and nitrate. The PUREX sludge has the highest concentration of iron oxide species and contributes low concentrations of phosphates to the tank waste. The modifications to the $BiPO_4$ modified sludge sample consists of the partial substitution of Nd and Eu (as spectroscopic probes) for La and the introduction of small amounts of Ti, Al, and Fe to simulate actual

9

sludge samples. The composition of sludge simulant samples is described in greater detail in a previous report (10). The results as a function of time are shown (along with the $BiPO_4$ results) in Figure 1. The different patterns of leaching with time and base concentration clearly demonstrate that the nature of the sludge does have an impact on the progress of the leaching.

If we consider the maximum percentage of americium leached from each of the sludge samples as a function of the base concentration (Figure 2), we find the widest spread between the sludge types at 1 M NaOH, that leaching of americium from the Redox sludge is most dramatically effected by [NaOH], that the differences between the sludge types is diminished as the total percent leached rises with [NaOH], and that 10-15 % of americium is leached from Redox or PUREX without the oxidant while less than 1% of americium is leached from $BiPO_4$ or $BiPO_{4\ modified}$ in the absence of oxidant. The differences between $BiPO_4$ and the Redox/PUREX samples could be a reflection of the comparative solubility of metal oxide/hydroxide solids vs. phosphates/fluorides. These results also demonstrate some of the attendant complexities introduced by the composition of these diverse solid mixtures, though it is clear that higher concentrations of base lead to greater mobilization of americium from all sludges in the presence of persulfate or permanganate.

Oxidative alkaline leaching with potassium permanganate ($KMnO_4$). The results of the leaching of americium by NaOH in the presence of $KMnO_4$ from the $BiPO_4$ sludge are summarized in Table 2. In the absence of $KMnO_4$, more than 99% of americium remained on the sludge after leaching with 1-5 M NaOH for 50 hours at 25°C (K_d =

20,000-80,000 ml/g) and 5 hours at 70°C (K_d = 10,000-16,000 ml/g). This expected result is fully consistent with the known chemistry of trivalent actinides in alkaline media. Sorption of Am(III) on the sludges is often nearly quantitative (as indicated in the loading experiments). Furthermore, the hydroxides, fluorides (present in $BiPO_4$ sludges), and phosphates of Am(III) are known to have very low solubility in neutral to basic solutions (12, 13), hence the intrinsic insolubility of Am(III) in discrete crystalline phases should also inhibit its solubility.

Introduction of $KMnO_4$ into the leachate results in a significant percentage of americium (10% - 50%) being removed from the sludge relatively quickly. In all cases, attainment of a steady-state occurred within less than 30 minutes. Increasing the temperature has a minimal effect on the percent leached by permanganate. The percentage leached increases with the concentration of NaOH, but is only slightly increased by raising the temperature. If the system is achieving a true steady state in these experiments, this result implies either that Am(III) is no longer the dominant oxidation state in the solution phase, or that a specific association between Am(III) and a mineral phase that dissolved in alkaline permanganate in this sludge simulant was responsible for Am(III) retention in the sludge sample. The use of tracer concentrations of americium in the experiments prohibits a direct determination (for example, by spectrophotometry) of the oxidation state of americium in the leachate. Typical radioanalytical techniques for actinide oxidations state characterization (14) would likewise prove unsuitable because of the strongly oxidizing characteristics of americium in its higher oxidation states. Without direct demonstration of oxidation, it still is apparent that oxidation of Am(III) is the most reasonable explanation for these observations.

It was observed that, the amount of americium in the $KMnO_4$ leachate reached a plateau and remained unchanged for many hours. Since the amount of oxidants (0.1 M $K_2S_2O_8$ or $KMnO_4$) is in large excess with respect to the amount of americium on the sludge, the appearance of a "plateau" seems difficult to explain. Moreover, visual identification of excess oxidants was difficult because the color of the leaching solution became so intensely dark after the first washing, probably resulting from a mixture of manganese species (purple MnO_4^-, dark green MnO_4^{2-}, brown $MnO_2(s)$, etc.) and dissolved sludge matrix components (chromium, iron and rare earths). To provide further insight into the leaching process and understand the "plateau" in the leaching efficiency, a consecutive second batch washing experiment was conducted. The supernatant containing americium leached in the first contact was removed from the tubes. Four ml of fresh solution with 0.1 M $KMnO_4$ and appropriate concentration of NaOH was added to the tubes. Again these were shaken for a period of time and aliquots of supernatant were taken and analyzed by LSC.

The results of the second washing (Figure 3) indicate that additional amounts of americium are leached from the sludge by fresh solutions of $KMnO_4$/NaOH. In fact, nearly 90% of total americium could be leached by $KMnO_4$/5 M NaOH with two "fresh" washings. These results suggest that the "excess" oxidants might gradually be consumed by other reactions including self-decomposition. There could be many components in the sludge that can catalyze such reactions. As a result, stepwise additions of the oxidant should be more effective in leaching americium from the sludges than one addition of all the oxidant.

Oxidative alkaline leaching with sodium ferrate (Na_2FeO_4). The results for leaching of americium from the $BiPO_4$ sludge by sodium ferrate are summarized in Table 3. It should be mentioned that, in contrast to the permanganate and persulfate experiments, the sodium ferrate was added as solid Na_2FeO_4, the amount of which would have been equivalent to 0.1 M in the suspension if it were dissolved completely. The results indicate that, although potassium ferrate is a strong oxidant and has been reported to oxidize chromium(III) to chromate in alkaline solutions very effectively (2), little americium was leached by $NaOH/Na_2FeO_4$. This was evidenced by the lack of color change of the supernatant over time: with the persulfate samples, the leaching of Cr(III) from the sludge is accompanied by a color change of the supernatant from colorless to green. This was confirmed by looking at the UV/vis spectrum of the solution. A broad peak at *ca* 370 nm is observed, corresponding to Cr(III).

Discussion

Steady-state Leaching Conditions. Significant amounts of americium are leached from all sludges by persulfate. Data on the leaching of americium by persulfate show distinct patterns for different sludges (Figure 1). The patterns of americium leaching shown in Figure 1 must derive in some manner from the differences in sludge composition, whether chemical factors or particle size/surface area mediated. Because the $BiPO_4$ process relied on coprecipitation of actinides in $BiPO_4$ and LaF_3 solid phases, these sludge simulants are dominated by these species. Our prior analysis indicated that these samples (both $BiPO_4$ and $BiPO_4$ modified) contained 5.3-7.6% by weight Cr, 7.2 % Mn and minimal Fe. The general similarity of americium leaching (from $BiPO_4$ and

BiPO$_4$ $_{modified}$) results indicate that the substitution of probe atoms (Nd and Eu) has little effect on americium leaching. The Redox sludge, derived from the effluents of solvent extraction from concentrated Al(NO$_3$)$_3$, is dominated by Al$_2$O$_3$, but also contains 3.8 % Cr, 5.1% Fe, and 1.1% Mn. The PUREX sludge simulant is primarily oxides of iron with lesser amounts of Al$_2$O$_3$, minimal Cr plus 2.2% Mn. Each simulant also carries 12-16% Na. In interpreting these results, it is important to recognize that in these biphasic experiments there are numerous potential pathways by which americium can be mobilized from the sludge samples.

The leaching of americium from the Redox sludge shows the greatest mobilization of americium of any of the three sludge samples at low base concentration (Figure 1c). The pattern of americium leaching in this system is also distinguished by the rapid decline in the amount of mobilized americium beyond 4 hours contact at low base concentration. At the higher base concentrations, more americium remains in solution for a longer period of time.

As noted previously, the defining characteristic of the Redox sludge simulant is the content of aluminum (by weight): 25.4% (Redox), 0% (BiPO$_4$), ≤ 3.9% (modified BiPO$_4$), and < 0.2% (PUREX) (10). One possible interpretation of these observations is that americium leaching may be a result of close association between Al$_2$O$_3$ and oxidizable components like Cr$_2$O$_3$ in this sludge simulant. The alkaline oxidative treatment causes rapid initial disruption of the sludge matrix, mobilizes Al and Cr from the sludge to the solution phase, and allows oxidation of americium, which remains in the solution phase while it remains in an oxidized condition. At high aluminate concentration the formation of polyaluminate anions becomes more likely (21). Such organization of

aluminate anions could lead to the formation of colloids on which americium species would be readily sorbed (22). Reprecipitation of the temporarily dissolved Al could account for the comparatively rapid redeposition of americium from the sludge. The tendency of AlO_2^- to remain soluble (and monomeric) should increase with increasing [NaOH], hence the oxidized/mobilized americium remains in the solution phase for a longer period at higher [NaOH].

A previous study of the leaching of U(VI) from these four sludge simulants (8) indicated that the chemical environments of U(VI) in the sludges are different. Data obtained by Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS) suggest that U(VI) is probably incorporated into the matrix of $BiPO_4$ and PUREX sludges, but could possibly exist as discrete hydrous oxides in the Redox sludge. Use of tracer amounts of americium in the present work does not allow the characterization of americium in the sludges by EXAFS. However, the distinct differences in the rate of leaching of americium from $BiPO_4$ and the patterns of "redeposition" (as compared with the other sludge samples) support the hypothesis that Am(III) is associated with phosphate in the $BiPO_4$ sludges. Rai *et al.* have characterized the low solubility of $AmPO_4$ under environmental conditions (12).

Having examined the leaching of americium from the $BiPO_4$ sludge by both persulfate and permanganate as a function of time, [NaOH], and temperature, we have an opportunity to assess the comparative influence of these parameters on americium leaching in this system. These data are shown in Figure 4. The values plotted in the case of permanganate represent steady-state concentration of americium in the solution phase (which was stable during the 20 hour observation period) while the corresponding

persulfate data are the maximum concentrations. The increase in temperature appears to have no statistically significant effect on the amount of americium leached in either system. The close coupling of the percent americium leached by the two oxidants strongly suggests that the amount of americium released is governed more strongly by the nature of the solid substrate than the power of the oxidant. It suggests predominance of a mechanism involving disruption of the solid matrix by the oxidant, which releases americium to the solution phase wherein Am(III) is then converted to a more soluble form. Furthermore, the similarity of the results in permanganate and persulfate implies that the byproducts of Cr oxidation ($MnO_{2\ (s)}$, $SO_4^=$) do not impact significantly the solubility of americium in the alkaline wash solution.

Leaching kinetics and possible mechanisms. The qualitative impression of the relative ease of leaching americium derived from visual inspection of the data in Figure 1 is that the rates of americium leaching increase in the order $BiPO_4 <$ Redox < PUREX. If we take the maximum percent leached in each plot as A_∞ and format the data as A_∞- A (using the tabulated percentages), a semilogarithmic plot of (A_∞- A) as a function of time conforms to a linear relationship, indicating that an apparent first order rate process describes the release of americium from the sludge samples. For the PUREX samples, a limiting slope was determined, that is, a slope was calculated using the first two data points. For the other sludge samples, each curve was characterized by 3-5 experimental points. The resulting rate constants are shown in Table 4. The derived rate constants for $BiPO_4$ and $BiPO_{4\ modified}$ leach studies overlap at the $\pm 3\sigma$ uncertainty level at 3 M and 5 M NaOH, confirming that the modification has no significant impact on the rate of americium leaching by persulfate. In 3 M NaOH, the rates of release of americium from

the PUREX is twice that from Redox, which is in turn 4-5 times faster than that seen from the $BiPO_4$ sludge. Each sludge demonstrates a slightly different dependence on the base concentration, the effect being most pronounced in PUREX while the leach rate from $BiPO_4$ is nearly independent of [NaOH].

Assuming that americium dissolution is a result of its oxidation (rather than specific mineral association), the possible species are Am^{4+}, AmO_2^+, and AmO_2^{2+}. In acidic solutions, all three of these species are powerful oxidants with potentials decreasing in the order $Am^{4+} > AmO_2^{2+} > AmO_2^+$. Redox potentials for americium in alkaline solution have not been measured. By analogy with other tetravalent actinides (Th^{4+}, U^{4+}, Pu^{4+}, Np^{4+}), Am^{4+} should exhibit low solubility in alkaline solutions, hence its presence in the solution phase in the absence of solubilizing complexants like EDTA is considered unlikely. We are left to conclude that either AmO_2^+ or AmO_2^{2+}(or both) are present in the solution phase (presumably as hydroxide complexes) while the oxidant is present. Our prior work on neptunium speciation (23) has established the comparative redox stability and solubility of the respective tetrahydroxides of penta- and hexavalent actinides in concentrated base solutions.

The exact reaction pathway(s) and mechanism of the oxidation/solubilization reactions are not clear from these experiments due to the complexity of the americium species in basic media and that of the sludge simulant samples. However, if we assume the hydroxides, $Am(OH)_3$ and AmO_2OH, are dominant, the oxidation of Am(III) in basic media can be represented by Equation 2:
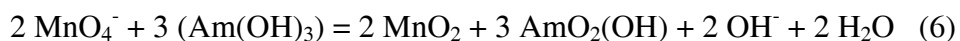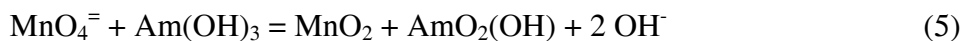
$$Am(OH)_3 + 2OH^- \rightarrow AmO_2OH + 2H_2O + 2e^- \tag{2}$$
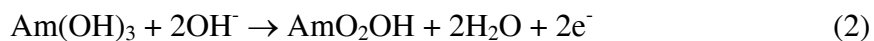
A standard potential (1.0 M NaOH) for reaction 2 has been calculated ($E° = +0.5V$) based on standard potentials in 1.0 M acid ($E° = 1.72$ V) (24), but no experimental value exists. Equation 2 indicates that higher concentration of NaOH would facilitate the oxidation. The prospective corresponding reaction for conversion of Am(III) to Am(VI) is:

$$Am(OH)_3 + 3OH^- \rightarrow AmO_2(OH)_2 + 2H_2O + 3e^- \qquad (3)$$
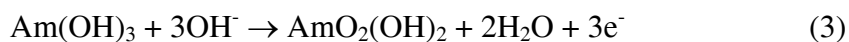
for which the estimated potential value is +0.6 V (24).

If one considers the net thermodynamic equilibrium for the manganese-americium system in concentrated basic solutions (assuming Am(V) as the probable product), the following possible equilibria are obtained:

$$2\ MnO_4^- + Am(OH)_3 + 2\ OH^- = 2\ MnO_4^= + AmO_2(OH) + 2\ H_2O \qquad (4)$$

$$MnO_4^= + Am(OH)_3 = MnO_2 + AmO_2(OH) + 2\ OH^- \qquad (5)$$

$$2\ MnO_4^- + 3\ (Am(OH)_3) = 2\ MnO_2 + 3\ AmO_2(OH) + 2\ OH^- + 2\ H_2O \quad (6)$$

The first equilibrium (Mn(VII)/Mn(VI)) is favored by excess base while the reaction ending in MnO_2 are inhibited by excess base. We have furthermore observed that the Mn(VII)/Mn(VI) reaction (Equation 4) is complete within 24 hours in 3 M NaOH, but much slower in 1 M NaOH. We speculate that the initial mobilization of americium from the sludge phase is a result of a process like that described in equation 4, thus favored by

increased concentration of base. With time, this reaction decreases in importance as MnO_4^- is converted to MnO_4^{2-} with further changes inhibited by a kinetic barrier to further reaction solubilitysuch as dissolution, structural rearrangements, etc.

Though "kinetically-challenged", the persulfate system has an adequate thermodynamic driving force to accomplish the oxidation of both Cr(III) and Am(III) oxidation readily (see Equation 1). The standard reaction for persulfate consumption is pH independent, hence the net reaction for americium oxidation is:

$$S_2O_8^= + Am(OH)_3 + 2\ OH^- = AmO_2(OH) + 2\ H_2O + 2\ SO_4^= \qquad (7)$$

The thermodynamics of this reaction are such that increased base concentration should promote oxidation of Am(III). This is consistent with the observed behavior of the system shown in Figure 1, where higher concentration of NaOH results in a higher percentage of americium leached. The oxidation/leaching stage of this reaction is consistent with the observed behavior of the system. The decline in americium leaching observed beyond 20 hours in the Redox samples most probably reflects the formation of aluminate colloids and the re-deposition of americium on the solid phase as discussed previously.

The lack of oxidative leaching of americium from the $BiPO_4$ sludge by $NaOH/Na_2FeO_4$ is more difficult to explain. Based on the thermodynamic driving force for oxidation and prior observations of actual sludge leaching performance (3), potassium ferrate is a thermodynamically-effective oxidant for Cr(III) (and by analogy with the persulfate and permanganate results, for Am(III) oxidation as well). However, it should be noted that because it was necessary to introduce sodium ferrate as the solid, the effective

concentration of ferrate in the suspension might be significantly lower than 0.1 M due to the limited solubility of sodium ferrate exhibited in NaOH. It is also conceivable that the complex nature of the chemical environment of americium in the sludge could place constraints on the reaction pathways and the kinetics of the redox reaction, possibly resulting in the ineffectiveness of sodium ferrate toward americium oxidation.

One particularly interesting aspect of this study is the "plateauing" that is observed in the mobilization of americium to the leachant phase. Based on the results of the secondary washing experiments, we assume that the oxidants may be consumed by processes such as self-decomposition catalyzed by varios sludge components. However, a more satisfactory explanation may require conducting experiments with macro-amounts of americium so that the oxidation state of americium can be directly determined by other techniques including UV/Vis/IR spectroscopy and EXAFS.

Acknowledgment

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Table 1. Leaching of americium from $BiPO_4$ sludge with $NaOH/K_2S_2O_8$ at 25 and 70 ^oC

Temperature (^oC)	Time (hours)	% americium in solution		
		1 M NaOH 0.1 M $K_2S_2O_8$	3 M NaOH 0.1 M $K_2S_2O_8$	5 M NaOH 0.1 M $K_2S_2O_8$
25	0.5	9.9	15.2	21.8
	1.0	8.4	13.1	24.3
	1.5	7.3	17.3	27.5
	3.0	6.1	22.6	31.5
	4.8	5.6	26.8	36.9
	19.7	8.2	34.8	41.1
	24.9	9.1	35.9	40.0
	28.7	8.4	20.0	36.1
70	0.5	10.7	30.7	41
	1.0	10.7	32.0	42.3
	1.5	11.2	32.9	41.7
	3.0	10.4	31.9	35.6

Table 2. Leaching of americium from $BiPO_4$ sludge with $NaOH/KMnO_4$ at 25 and 70 °C

Temperature (°C)	Time (hours)	1 M NaOH		3 M NaOH		5 M NaOH	
		Without $KMnO_4$	0.1 M $KMnO_4$	Without $KMnO_4$	0.1 M $KMnO_4$	Without $KMnO_4$	0.1 M $KMnO_4$
25	0.5	0.2	15.6	0.5	37.9	1.2	43.2
	1.0	0.2	14.7	0.3	38.2	0.4	38.3
	3.0	0.2	14.3	0.3	36.7	0.3	39.9
	22.0	0.2	11.6	0.2	33.2	0.4	40.7
	30.0	0.1	11.8	0.2	29.6	0.2	34.7
	44.0	0.1	10.5	0.2	29.4	0.3	38.2
	52.0	0.1	8.6	0.3	35.5	0.4	43.0
70	0.5		18.6		33.4		38.3
	1.0		19.1		38.1		46.9
	3.0		15.0		39.1		48.2

5.0	0.5	17.2	0.7	34.0	0.8	42.0

Table 3. Leaching of americium from $BiPO_4$ sludge with $NaOH/Na_2FeO_4$ at 25 and 95 ^oC

Temperature (^oC)	Time (hours)	% americium in solution					
		1 M NaOH		3 M NaOH		5 M NaOH	
		Without Na_2FeO_4	0.1 M Na_2FeO_4	Without Na_2FeO_4	0.1 M Na_2FeO_4	Without Na_2FeO_4	0.1 M Na_2FeO_4
25	10 mins	0.3	0.9	0.3	1.5	0.3	1.6
	3.0	1.2	1.5	1.2	1.9	1.2	1.9
	24.0	1.6	2.3	1.6	1.7	1.6	2.0
95	10 mins		1.3		2.2		2.0
	3.0		3.1		3.9		5.3
	24.0	0.2	2.7	0.7	3.6	1.3	3.9

Table 4. First Order Rate Constants for americium Leaching from Sludge Simulants by Alkaline Persulfate Solutions (0.1 M) (Uncertainties represent 95% confidence interval ($\pm 2\sigma$) − No uncertainties are indicated for PUREX results because they are limiting rates calculated from two experimental data points).

Sludge	1.0 NaOH	3.0 M NaOH	5.0 M NaOH
	k (hr^{-1})	k (hr^{-1})	k (hr^{-1})
$BiPO_4$	-	0.16 ($\pm$0.04)	0.34($\pm$0.05)
$BiPO_{4\ modified}$	-	0.21($\pm$0.05)	0.25($\pm$0.04)
Redox	0.50 ($\pm$0.03)	0.89($\pm$0.28)	1.14($\pm$0.10)
PUREX	-	1.64	3.07
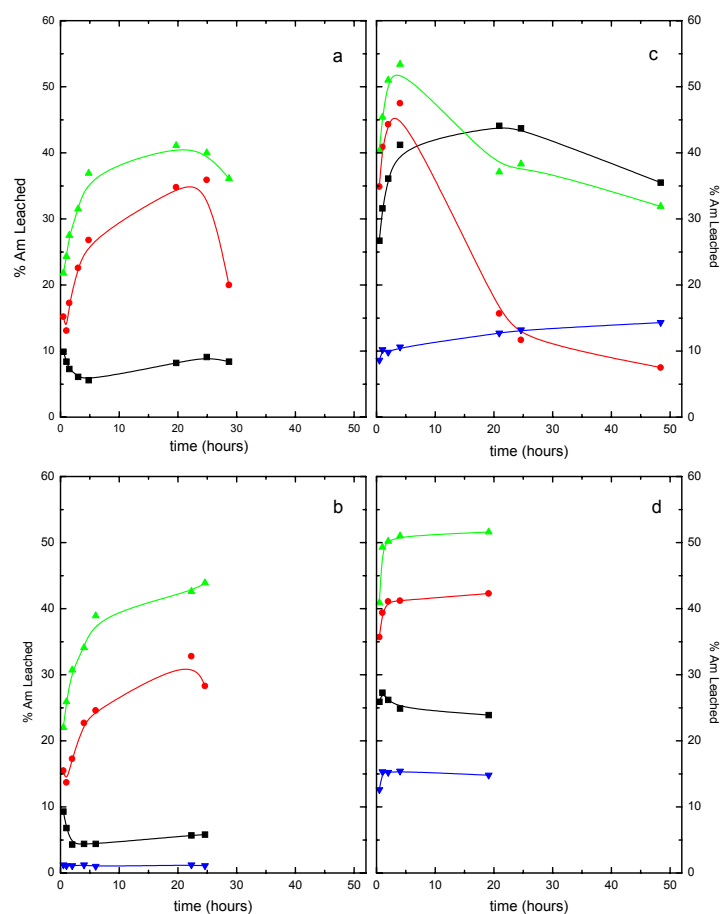
Figure 1. Leaching of americium from sludge simulants by 0.1 M $K_2S_2O_8$ in alkaline solutions: a - $BiPO_4$ sludge simulant; b - $BiPO_4$ modified sludge simulant; c- Redox sludge simulant; d - PUREX sludge simulant. Leachant: (*down triangle*) 5.0 M NaOH, no oxidant present; (+ Square) 1.0 M NaOH; (! circle) 3.0 M NaOH; (*up triangle*) 5.0 M NaOH.
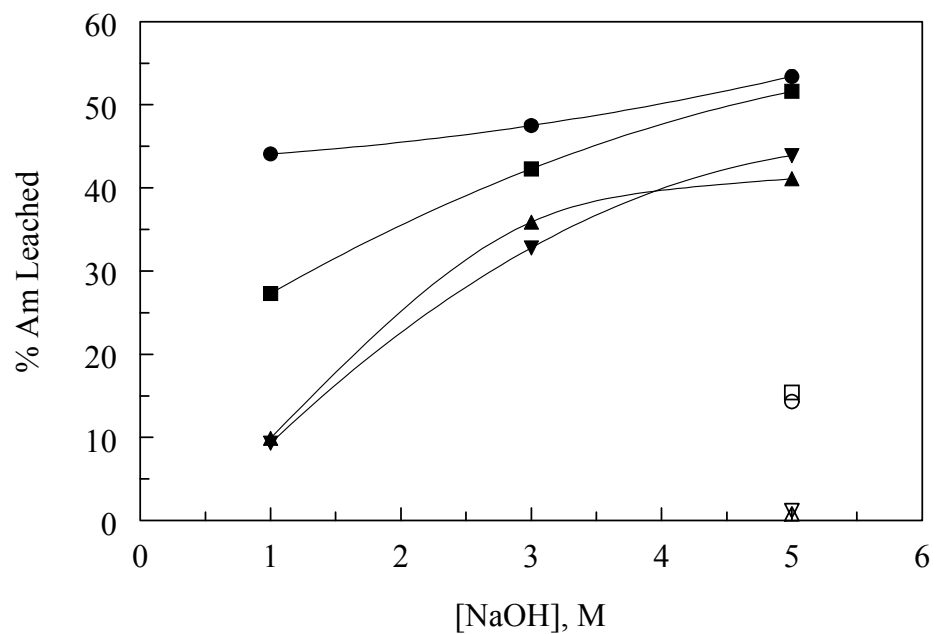
Figure 2. Leaching of americium from sludge simulants as a function of [NaOH]. Solid symbols (● ■): with 0.1 m potassium persulfate; open symbols (O ∇Δ): without potassium persulfate. (●O) Redox sludge; (■) PUREX sludge, (∇) BiPO$_4$ sludge modified; (Δ) BiPO$_4$ sludge.
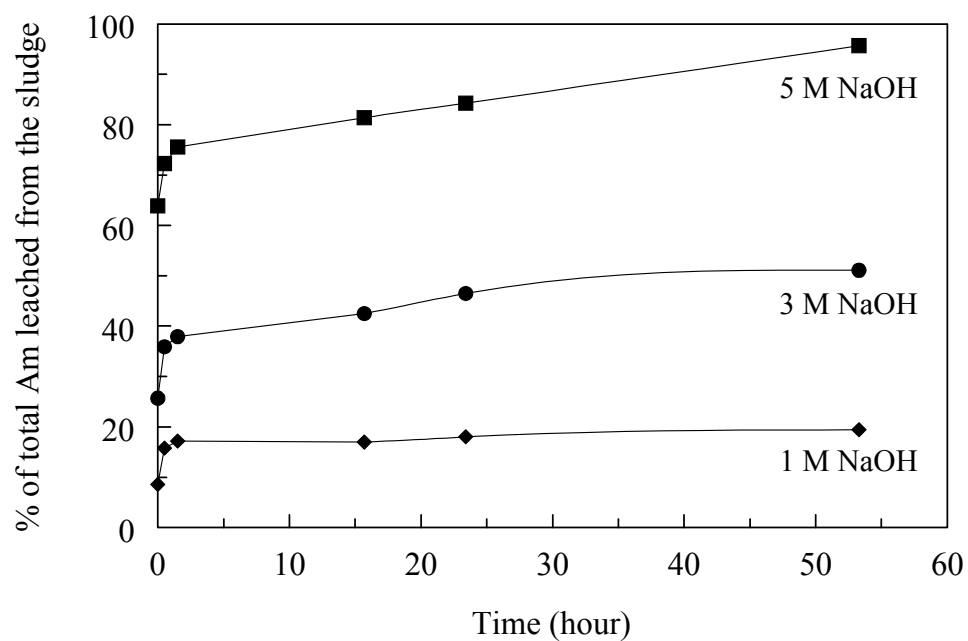
Figure 3. Second washing of simulated BiPO$_4$ sludge with NaOH/0.1 M KMnO$_4$ (percentage values represent TOTAL amount of americium leached during both washings)
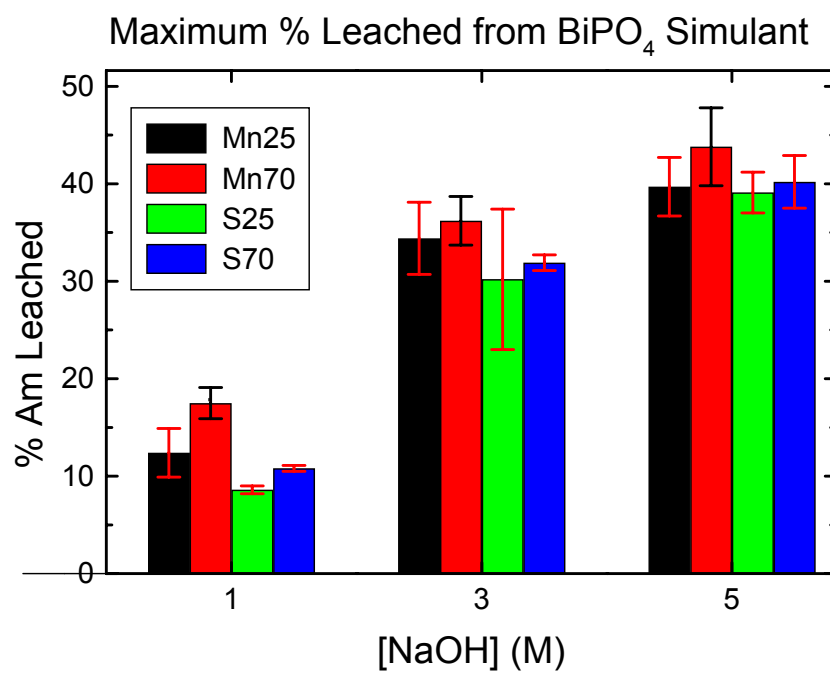
Figure 4. Maximum Americium Leaching from $BiPO_4$ Simulant by Permanganate and Persulfate as a Function of [NaOH] and Temperature.